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(54) **Process and apparatus for preparing thin films of polymers and composite materials on different kind of substrates**

(57) The present invention relates to a process and an apparatus for preparing thin films having a thickness of the order of the micrometer and formed of polyimides so-called FIPOL I, FIPOL II, FIPOL III on solid substrates of different kinds, particularly of glass, oxides of elements such as Si, Al, or elements such as Si, Ge, Ti, C and others, comprising the steps of: a) hard vacuum evaporation of the polymeric precursors following on the heating under thermal control conditions such as to assure a homogeneous evaporation rate; b) deposition of the vapours produced in a) on a chemical solid substrate which may be made of inorganic oxides, metals and non-metals so as to provide a homogeneous film on the whole surface concerned; c) stabilization of the film by heating in an inert atmosphere so as to provide a compact, homogeneous deposit of determined thickness.

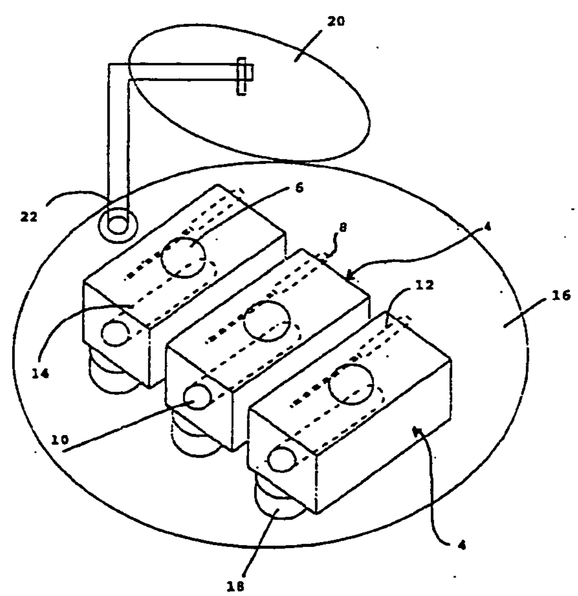


FIGURE 6

Description

The present invention relates to a process and an apparatus for preparing thin films of polyimide polymers, hereinafter referred to as FIPOL I, FIPOL II and FIPOL III for the sake of brevity, on a solid substrate of various chemical composition for the modification of chemical-physical surface characteristics of such a substrate. Particularly, solid substrates such as, for example, inorganic oxides such as glass, SiO_2, Al_2O_3 or metals such as Ti, Cu, Al or non-metals such as Si, C, Ge may be used. Said polyimide polymers differ in structure and morphology from the polyimides already chemically produced by Dupont De Nemours and by UBE and known under the trademarks KAPTON® and UPILEX®, even if they have similar chemical formula.

By way of example, the surface deposits provided by the described process may be advantageously used for the protection of metal objects since such a process allows homogeneous controlled-thickness films to be prepared irrespective of the geometric form and the nature of the substrate. As chemically inert polymeric films stable up to 400°C are concerned, the process allows the fields of application of said materials modified in their mechanical, electrical, optical surface characteristics to be advantageously extended.

Another field of application relates to the preparation of polyimide-metal surface deposits by one and only process of providing films having a typical conductivity of a semiconductor, then adapted in micro-electronics and electrostatics. Such a composite material is referred to as CONPOL (registered trademark by the Applicant) in the following description.

The above-cited fields of application of the invention are only some of the main fields indicated by way of a not limiting example of the invention since the process, the used materials, the organic, metal and organometal precursors, as described and claimed later on, may be advantageously used in any other equivalent field in which polyimide deposits modified or not by means of metals are produced on solid substrates to cause a permanent modification of the surface characteristics.

Processes of such a type are known. Particularly the process of the article of Salem et al, *(Journal of Vacuum Science & Technology,* A4 (3), 1986, page 369) relates to the preparation of polyimide films of the type FIPOL I to be deposited on various substrates by using a highly specific apparatus for controlling the process of evaporation which does not allow surfaces of large size or lower than some square centimetres to be treated. Also Pethe et al. *(Journal of Material Research,* Vol. 8, No. 12, 1993, page 3218) disclose a process for depositing polyimide films of the type FIPOL I by using a very expensive apparatus not adapted to the treatment of wide surfaces. Further processes such as those disclosed by Lamb et al. *(Lagmuir-* Vol. 4, 1988, page 249), Yamada et al. *(Journal of Vacuum Science & Technology,* Al 1 (5), 1993, page 2590), Iijma et al. *(Macromolecules,* Vol. 22, 1989, page 2944) have technical drawbacks which can be overcome only by specific research instruments and then are not adapted for a continuous industrial production.

The main object of the present invention is of overcoming the above-complained problems and limitations by a process which allows compact polyimide films such as the so-called FIPOL I, FIPOL II, FIPOL III and compositions thereof with metals to be provided by a controlled-thickness process for the modification of the chemical-physical surface characteristics of solid substrates of various kind without any limitations of the treated surface area.

A second object of the present invention is of providing deposits having half-insulation characteristics on varying-geometry substrates by one and only process.

A further object of the present invention is of providing polyimide films FIPOL I, FIPOL II, FIPOL III having no internal separation surfaces or cracks and exhibiting the same mechanical characteristics and the same surface tension values, chemical etching resistance and thermal endurance as the massive polyimide materials.

These and other objects can be achieved by a process for preparing surface deposits of polyimide polymers referred to as FIPOL I, FIPOL II and FIPOL III on a solid substrate of various nature, particularly those based upon inorganic oxide such as, for example, glass, SiO_2, Al_2O_3 or metals such as Ti, Cu, Al or non-metals such as Si, C, Ge, comprising the steps of:

a) hard vacuum evaporation of the polymeric precursors following on the heating under thermal control conditions such as to assure a homogeneous evaporation rate.

It was surprisingly found that the molar evaporation rate of both precursors (as for FIPOL I, benzentetracarboxylic dianhydride and 4,4'-oxydianiline; as for FIPOL II, biphenyltetracarboxylic dianhydride and 1,4-phenylendiamine-dianiline; as for FIPOL III, benzophenontetracarboxylic dianhydride and tetramethyl-p-phenylendiamine) is the same at the temperature of 180°C as shown in the diagrams of Fig. 7a relating to the evaporation rate of 4,4'-oxydianiline (ODA) and Fig. 7b relating to the evaporation rate of (benzentetracarboxylic dianhydride (PMDA).

b) deposition of the vapours produced in a) on a chemical solid substrate which may be made of inorganic oxides, metals and non-metals so as to provide a homogeneous film on the whole surface concerned.

c) stabilization of the film by heating in an inert atmosphere so as to provide a compact, homogeneous deposit of determined thickness.

Therefore, a first aspect of the invention provides that the heating for the evaporation of the precursors takes place under a temperature control system. Particularly, such a control is carried out by using a series of melting pots placed within a vacuum chamber and having a particular geometry and being provided with their own heating means for a controlled-temperature heating.

A second aspect of the invention provides the change of the distance between melting pot and substrate to be coated by a suitable mechanical device.

A third aspect of the invention provides the controlled evaporation of the polymeric precursors simultaneously to that of the organometal compositions, the low-melting-point metals, and other chemical compositions which can be sublimed.

A further aspect of the invention provides the polyimide film thickness control by controlling the evaporation time.

In order to achieve such objects and to provide the above-mentioned process the invention makes use of an apparatus including a vacuum chamber provided with a series of melting pots of suitable geometry for the evaporation of the precursors, such melting pots being provided with an automatic temperature control system, melting pot-substrate distance setting means, and evaporation time control means.

The main advantages provided by the process according to the present invention are:

(i) preparation of homogeneous films of stable polymers or compositions thereof with metals on substrates such as metals, inorganic oxides or non-metals of varied geometry under simple operative conditions;
(ii) capability of modulating the process so as to be able to vary the thickness of the film according to the evaporation time and the kind of the substrate;
(iii) providing such surface deposits without any limitation in the extension of the treated surface, without discontinuity or modifications of the chemical-physical characteristics of the deposited polymer.

Further characteristics and advantages of the invention will be more readily apparent from the following description of the apparatus and three examples showing by way of an indicative, not limiting example the process according to the invention with reference to the accompanying drawings in which:

Fig. 1 shows schematically and generally an elevation front view of the device according to the invention with the vacuum chamber and the vacuum system;

Fig. 2 shows still schematically an elevation front view of the melting pot system used for the evaporation of the precursors and supported by flange A of the device of Fig. 1;

Fig. 3 is still an elevation front view of the mechanical device supported by flange B of Fig. 1 for controlling the melting pot-substrate distance;

Fig. 4 is a side view of flange C of Fig. 1 with the thickness gauge and the vacuometer;

Fig. 5 is a top plan view of flanges B and C of Fig. 1;

Fig. 6 is a perspective view of the melting pot system of Fig. 2;

Fig. 7 is a diagram showing the evaporation rate of the precursors of FIPOL I vs. the temperature;

Fig. 8 is a diagram showing the homogeneity of the thickness of the FIPOL I deposit;

Fig. 9 is a diagram showing the thickness of FIPOL I vs. the time;

Fig. 10 is a microphotography made by electronic scanning microscopy of a FIPOL I deposit on silicium;

Fig. 11 is the IR transmission spectrum of FIPOL I deposited on a pellet of KBr;

Fig. 12 shows a diagram of the coefficient of friction vs. the applied load and the thermal treatment temperature for film of FIPOL I on 6000 Å thick silicium;

Fig. 13 shows a diagram of the surface resistivity of a deposit of CONPOL on SiO_2 vs. the time at different voltages;

Fig. 14 is the RBS spectrum of a CONPOL sample deposited on Si where the analysis beam is formed of protons energized at 1,5 MeV;

Fig. 15 is a schematic view of a continuously rotating mechanical device for coating cylindrical substrates;

Fig. 16 shows the diagram of the erosion rate in 40% HF of a glass cylinder before and after being coated with FIPOL I;

Figs. 17A and 17B compare two microphotographs made by an optical 10-magnification microscope and showing a deposit of FIPOL I and a deposit having the same thickness on the same substrate of KAPTON (registered trademark by DUPONT DE NEMOURS).

With reference to Figs. 1 to 6, the device for carrying out the process according to the invention essentially includes:

a conventional vacuum chamber 2 with six mouths having orthogonal axes and provided with flanges, to one of which, indicated at D, the vacuum system formed of a turbomolecular pump PT and a rotating pump PR is connected through a cold junction H, and

a series of melting pots 4 formed of parallelepipeds of ultrapure copper provided with a central cavity 6 in which a mixture of precursors is placed and with two through holes 8 and 10 receiving the vacuum thermocouple 12 and the heating tubular resistance 14, respectively, both connected to a thermal regulation unit carrying out the automatic control of the temperature and keeping the variation thereof within 1°C.

The melting pots are spaced apart regularly in a row with the interposition of ceramic spacers 18 on a support plate 16 of aluminium which is supported by flange A through further ceramic spacers 18' under the rotary shutter 20 fixedly connected to a vacuum-tight rotary tubular member 22 passing through the plate. Further passing tubular members 24 are provided for the connection to the power supply and the thermocouples. The geometric arrangement shown in Fig. 6 is, of course, indicating and not limiting as the active surface may be extended by using coupled melting pots.
The distance between melting pots and surfaces of the substrate to be treated can be set through a mechanical system illustrated in Figs. 3 and 5.
As can be seen in such figures, the substrate to be treated is placed on a sample carrying plate 26 which is slidable along two vertical guide rods integral with flange B and is moved by a worm screw 30 connected to a rotary member 32 near a vacuometer 40.
The evaporation of the precursors at 180°C is obtained with constant flow and unit mole ratio by putting both precursors in one melting pot. The vapours are deposited on the solid substrate to be treated so as to provide a homogeneous film on the whole surface concerned. Such a result takes place, for example, in case of deposits of FIPOL I on Si under the above-mentioned conditions.
A thickness gauge or profilometer, the head 36 of which is cooled by two anacondas (hoses) 38 for supplying cooling water, is supported by a vacuum-tight passing member on flange C (Fig. 4). A vacuometer is indicated at 42.
The thicknesses of the film deposits shown in Fig. 8 are obtained after an evaporation treatment of 6 hours and can be detected by the profilometer after heating at 250°C in a nitrogen atmosphere. Up to a distance of 4 cm from the central axis of evaporation there is no thickness variation in case of an arrangement of three melting pots located on a strip of 8 cm, as shown in Fig. 6.
Fig. 8 shows that the thickness variation of the film is by 20% as a maximum at a distance of 10 cm.
The mechanical apparatus of Fig. 15 is capable of coating cylindrical substrates by continuously rotating the substrate within the vacuum chamber. As can be seen, the cylindrical substrate to be coated 44 is supported by a bush 46 of teflon® connected to a wire 48 of harmonic steel. The latter is guided by a steel tube 50 and is connected at the opposite end to a bush 52 of musmetal integral with the rotation pin of a rotary vacuum-tight passing member 54 externally connected to a motor 56.

The following examples explain in a better way the characteristics of the process and the products obtained according to the invention.

EXAMPLE 1

The vacuum chamber of Fig. 1 is used for the surface treatment of samples having a surface area of about 100 cm^2. The precursors of polyimide FIPOL I (benzentetracarboxylic dianhydride and 4,4'-oxydianiline) are placed into three melting pots shown in Figs. 2 and 6. The distance between melting pots and the surface of the substrate to be treated may be gradually set by the mechanical device formed of plate 26, rods 28 and worm screw 30.
In this example the substrate is polycrystalline silicium. Said melting pots were preliminarily filled with benzentetracarboxylic dianhydride, heated at different temperatures up to a maximum of 220°C, and kept at each temperature for a period of 120 minutes. The used substrate was a quartz crystal acting as sensor of the deposited thickness according to the oscillation frequency variations. The deposition rates according to the temperature were thus obtained as shown

in Fig. 6, curve a.
The same process was applied to the other precursor and curve b of Fig. 7 was obtained.

By comparing said two curves it can be seen that the temperature of 182°C is the experimental parameter at which the molar evaporation rates of the two precursors are the same.
Deposits of the two precursors in times varying from 70 to 360 minutes were carried out on the substrate of polycrystalline silicium. The diagram of the thickness vs. the time is shown in Fig. 9.
The homogeneity of the deposit was proved by carrying out measurements of thickness transversally to the central axis of evaporation, the three melting pots being placed on the same axis over a length of 8 cm. The result is shown in Fig. 8 in which the distance between melting pot and substrate is 6 cm.
Fig. 10 shows a photogram obtained by electronic scanning microscopy showing the surface magnified 23739 times without discontinuities or cracks (the scratch which may be seen was intentionally made as reference for the focusing).
The comparison between FIPOL I and KAPTON (registered trademark by Dupont de Nemours) as far as the morphological surface homogeneity is concerned is shown in Figs. 13A and 13B in which two pictures obtained by an optical 10-magnification microscope (1 graduation of the ruler corresponds to 10 microns) are shown.
Fig. 11 shows the IR spectrum of a deposit of FIPOL I on the surface of a pellet of KBr under the above-mentioned conditions relating to the evaporation of the precursors and the next thermal treatment.
The adhesion between the polymer and the substrate of silicium for samples treated at different temperatures was proved by scratch tests. The results illustrated in Fig. 12 show the reduction of the coefficient of friction with the increase of the temperature of the stabilization treatment as well as the strong reduction of the critical load when passing from 250°C to 300°C.
The values of the coefficient of friction and the critical load are shown in Table 1. The critical load has been evaluated through the examination of the different sample by an optical microscope.

TABLE 1

Treatment temperature	Coefficient of friction	Critical load
250°C	0.15	110 g
300°C	0.16	10 g
350°C	0.13	10 g

EXAMPLE 2

A deposit of a composite material FIPOL I-Pt was carried out on polycrystalline silicium with simultaneous deposition of the precursors (benzentetracarboxylic dianhydride and 4,4'-oxydianiline) and Pt (1,5 $C_8H_{12})C_{12}$. The Pt composition was sublimed in advance without other components and an evaporation rate of 5 nm/h at 205°C was obtained. A film on a sapphire was produced through simultaneous evaporation of said composition, placed in the central melting pot at 205°C, and the two precursors of FIPOL I, placed in the side melting pots at 182°C. Such a film subjected to a thermal treatment under N_2 for 2 hours at 250°C is a homogeneous dispersion of Pt in FIPOL I (Fig. 7) as ascertained by RBS analysis (Rutherford Backscattering Spectrometry). The atomic ratio between Pt and C is about 1/28.

Such a material was referred to as CONPOL. Samples of such a material were subjected to measurements of electrical surface resistivity and the results are shown in Fig. 14. The surface resistivity becomes stable after about 60 minutes and reaches the typical values of the half-insulating materials. The non-ohmic characteristics are shown in the same figure.

EXAMPLE 3

Films of FIPOL I on solid substrates of cylindrical form were deposited by the mechanical motorized apparatus (Fig. 15) already described into detail and operating with the vacuum chamber of Figs. 1-4. It should be appreciated that the mechanical system allows cylindrical substrate to be continuously rotated at a speed varying from 10 to 100 rpm, while the inclination of the steel guide tube 50 allows also the base of the cylindrical substrate 44 to be coated. Particularly under the conditions of Example 1 and at a rotation speed of 60 rpm a deposit of FIPOL I on a glass cylinder of 8 mm diameter and 4 mm length was produced. The thickness homogeneity of the deposit is assured by the continuous rotation of the cylindrical substrate about its own axis. After a thermal treatment at 250°C under a N_2 atmosphere for 2 hours the cylinder was subjected to a chemical etching in a 40% solution of hydrofluoric acid. The curve of Fig. 14 shows the weight loss according to the immersion time. In the same figure there is shown the same relationship for a like glass cylinder not coated with polyimide.

The results shown in the figures confirm the advantages of the process for providing surface deposits of the present invention.

Particularly the preparation of the surface deposits of composite materials finds a wide application with reference to parts of radiation detectors such as the microstrip gas chambers and the microgap chambers since it is possible to deposit films on a very great number of different substrates: the polymer film assures a chemical-physical stability for the substrate against corrosion and damages due to radiations by modifying the wettability and the electrical-mechanical surface characteristics.

The present invention is described and illustrated on the base of a preferred embodiment thereof. It should be understood that a number of construction modifications and changes may be made by those skilled in the art without departing from the scope of the present industrial invention as defined in the following claims.

Claims

1. A process of depositing thin films of polyimides through evaporation of the components, comprising the steps of:

   a) hard vacuum evaporation of the polymeric precursors following on the heating under thermal control conditions such as to assure a homogeneous evaporation rate;
   b) deposition of the vapours produced in a) on a chemical solid substrate which may be made of glass, inorganic oxides, metals and non-metals so as to provide a homogeneous film on the whole surface concerned;
   c) stabilization of the film by heating in an inert atmosphere so as to provide a compact, homogeneous deposit of determined thickness.

2. The process of claim 1, characterized in that the thickness of the film is controlled by controlling the evaporation time.

3. The process of claim 1, characterized in that the evaporation of the polymer precursors takes place simultaneously and at the same temperature, with constant flow and unit molar ratio.

4. The process of claim 3, characterized in that said temperature is about 180°C (± 2).

5. The process of the preceding claims, characterized in that the polymer precursors are benzentetracarboxylic dianhydride and 4,4'-oxydianiline.

6. The process of the preceding claims, characterized in that the polymer precursors are biphenyltetracarboxylic dianhydride and 1,4-phenylendiamine-dianiline.

7. The process of the preceding claims, characterized in that the polymer precursors are benzophenontetracarboxylic dianhydride and tetramethyl-p-phenylendiamine.

8. A process for the deposition of thin films of polyimide-metal composite materials comprising the steps of:

   a) hard vacuum evaporation of the polymeric precursors simultaneously with the organometal compositions, low-melting-point metals, and other chemical compositions which can be sublimed, said precursors and said compositions and/or metals being heated under thermal control conditions such as to assure a homogeneous evaporation rate.
   b) deposition of the vapours produced in a) on a chemical solid substrate which may be made of glass, inorganic oxides, metals and non-metals so as to provide a homogeneous film on the whole surface concerned.
   c) stabilization of the film by heating in an inert atmosphere so as to provide a compact, homogeneous deposit of determined thickness.

9. The process of the preceding claims, characterized in that the film exhibits the chemical-physical characteristics of the massive material under thermal treatment in an inert atmosphere.

10. A device for carrying out the process of claims 1 and 8, comprising a vacuum chamber adapted to contain a series of melting pots of suitable geometry for the evaporation of the precursors, each melting pot being provided with its own heating system with automatic temperature control, means for varying the distance between the melting pot and the substrate to be treated and means for controlling the evaporation time being also provided.

11. The device according to claim 10, characterized in that the geometry and the number of the melting pots change in order to provide deposits of varying thickness and composition or in case of substrate surfaces of particular geometry.

12. A mechanical motorized device for continuously rotating cylindrical substrates to be coated with a homogeneous film, characterized in that the rotary motion is transmitted to the cylindrical substrate to be coated through a harmonic steel wire guided within a steel tube, said wire being connected at one end to a rotary pin and at the other end to a bush supporting said cylindrical substrate to be coated.

13. The mechanical device of claim 12, characterized in that the steel tube guiding the harmonic steel wire is inclined to the driving shaft at the end which carries the bush supporting the cylindrical substrate to be coated.

14. A polymer material prepared from the polyimide precursors such as benzentetracarboxylic dianhydride and 4,4'-oxydianiline, characterized in that it is a homogeneous thin film having no internal separation surfaces or cracks and exhibiting the same mechanical characteristics and the same surface tension, resistance to the chemical etching and thermal endurance as the massive polyimide material.

15. A polymer material prepared from the polyimide precursors such as biphenyltetracarboxylic dianhydride and 1,4-phenylendiamine-dianiline, characterized in that it is a homogeneous thin film having no internal separation surfaces or cracks and exhibiting the same mechanical characteristics and the same surface tension, resistance to the chemical etching and thermal endurance as the massive polyimide material.

16. A polymer material prepared from the polyimide precursors such as benzophenontetracarboxylic dianhydride and tetramethyl-p-phenylendiamine, characterized in that it is a homogeneous thin film having no internal separation surfaces or cracks and exhibiting the same mechanical characteristics and the same surface tension, resistance to the chemical etching and thermal endurance as the massive polyimide material.

17. Polyimide-metal composite materials having the electrical characteristics of the half-insulating materials provided by simultaneous evaporation of the polyimide precursors and the metal.

18. The process for the deposition of thin films of claims 1 and 8, characterized in that it may be used for providing thin films on solid substrate without any limitation as far as the chemical composition, the geometric form and the surface to be coated is concerned.

19. Use of the surface deposits provided by the processes of the preceding claims as chemically inert films against corrosion and deterioration due to environmental conditions, or as protection of devices subjected to particular physical stress.

20. Use of the surface deposits provided by the processes of the preceding claims and havinng the surface resistivity typical of the half-insulating materials as detectors of particles and radiations on electrical and electronic devices.

21. Coating thin film provided by hard vacuum evaporation of the components, characterized in that it is formed of a mixture of polyimides with components not greater than 30% in weight such as to modify the chemical-physical characteristics of said massive polyimides.

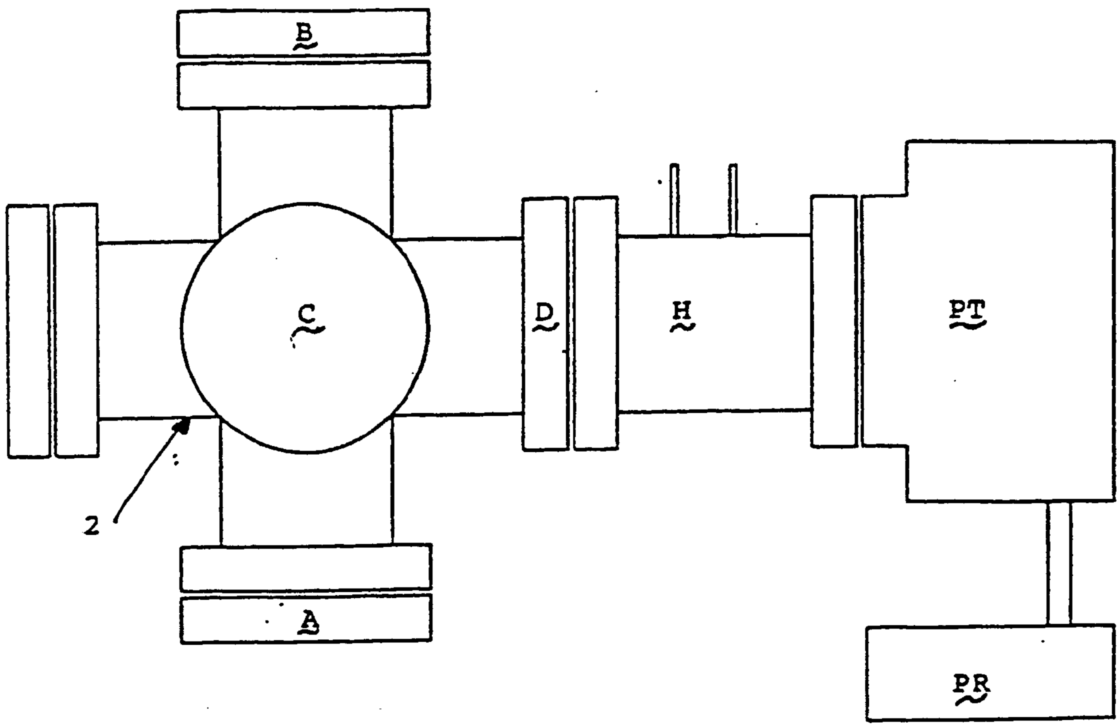


FIGURE 1

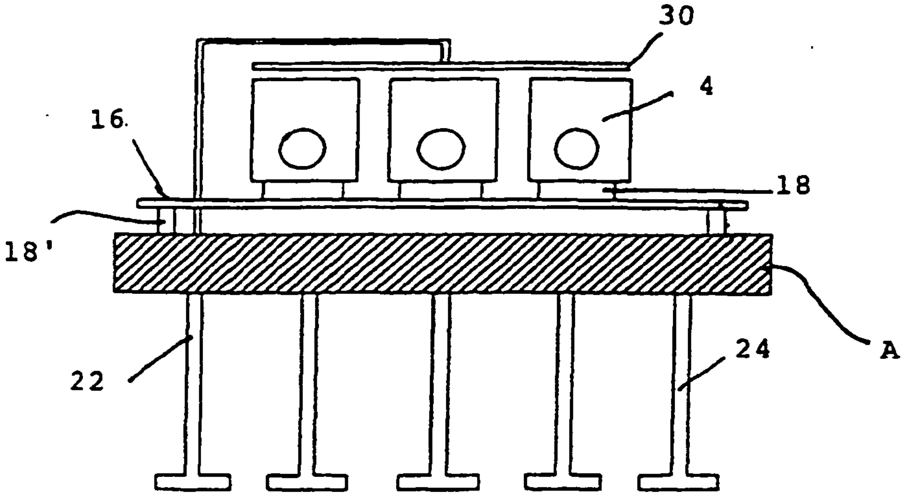


FIGURE 2

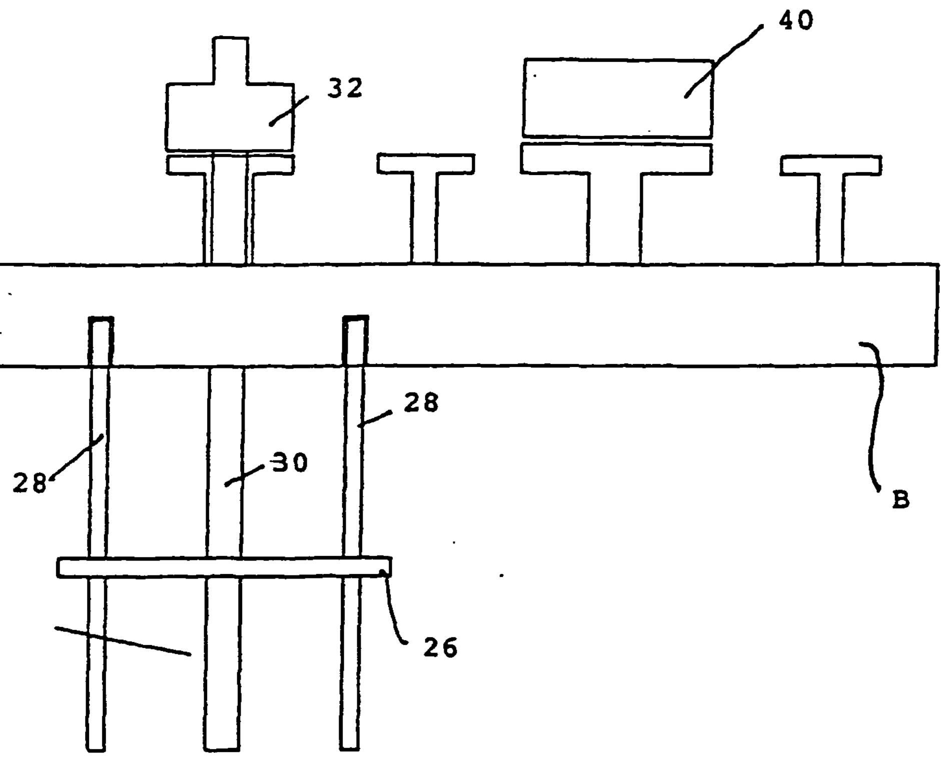


FIGURE 3

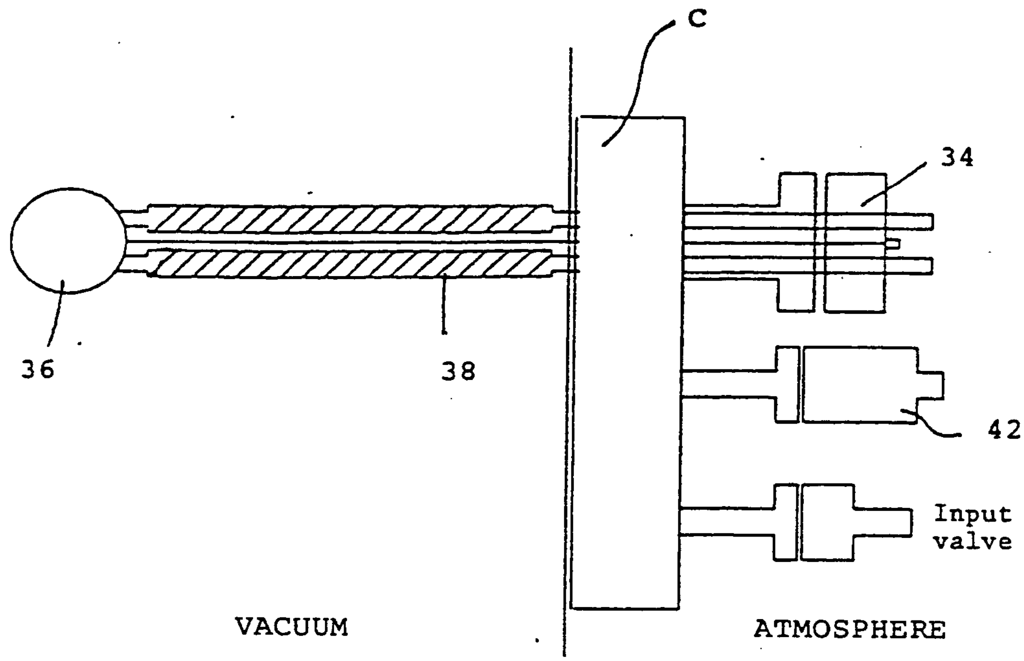


FIGURE 4

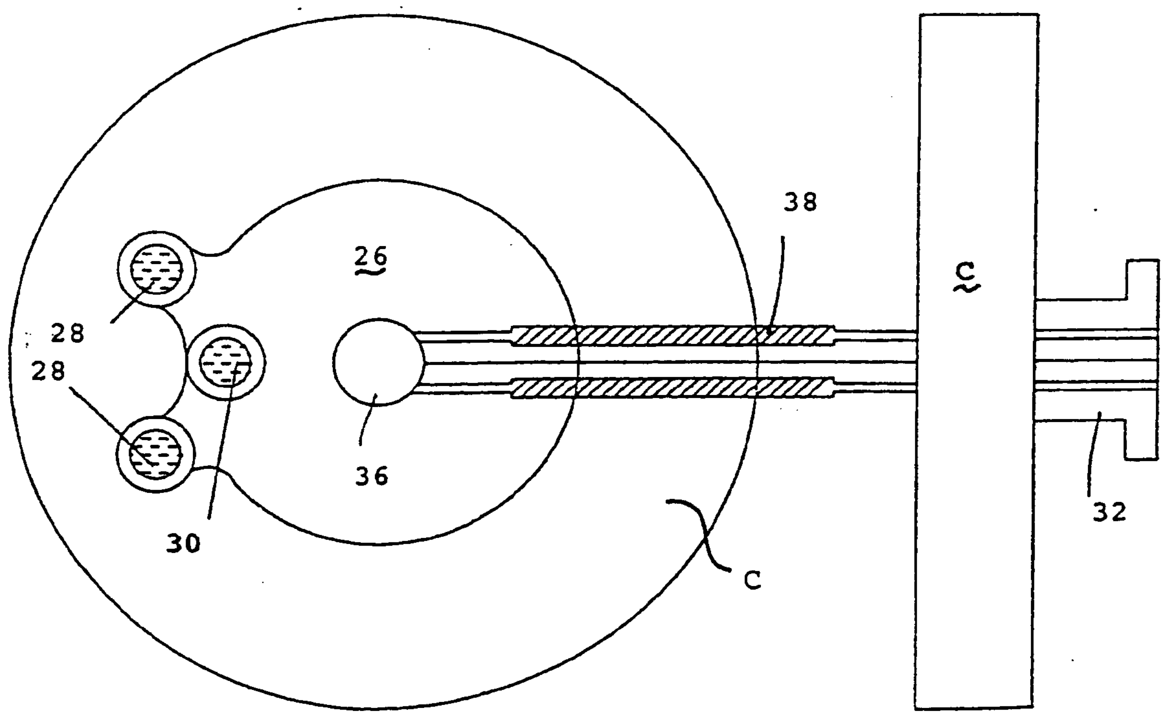


FIGURE 5

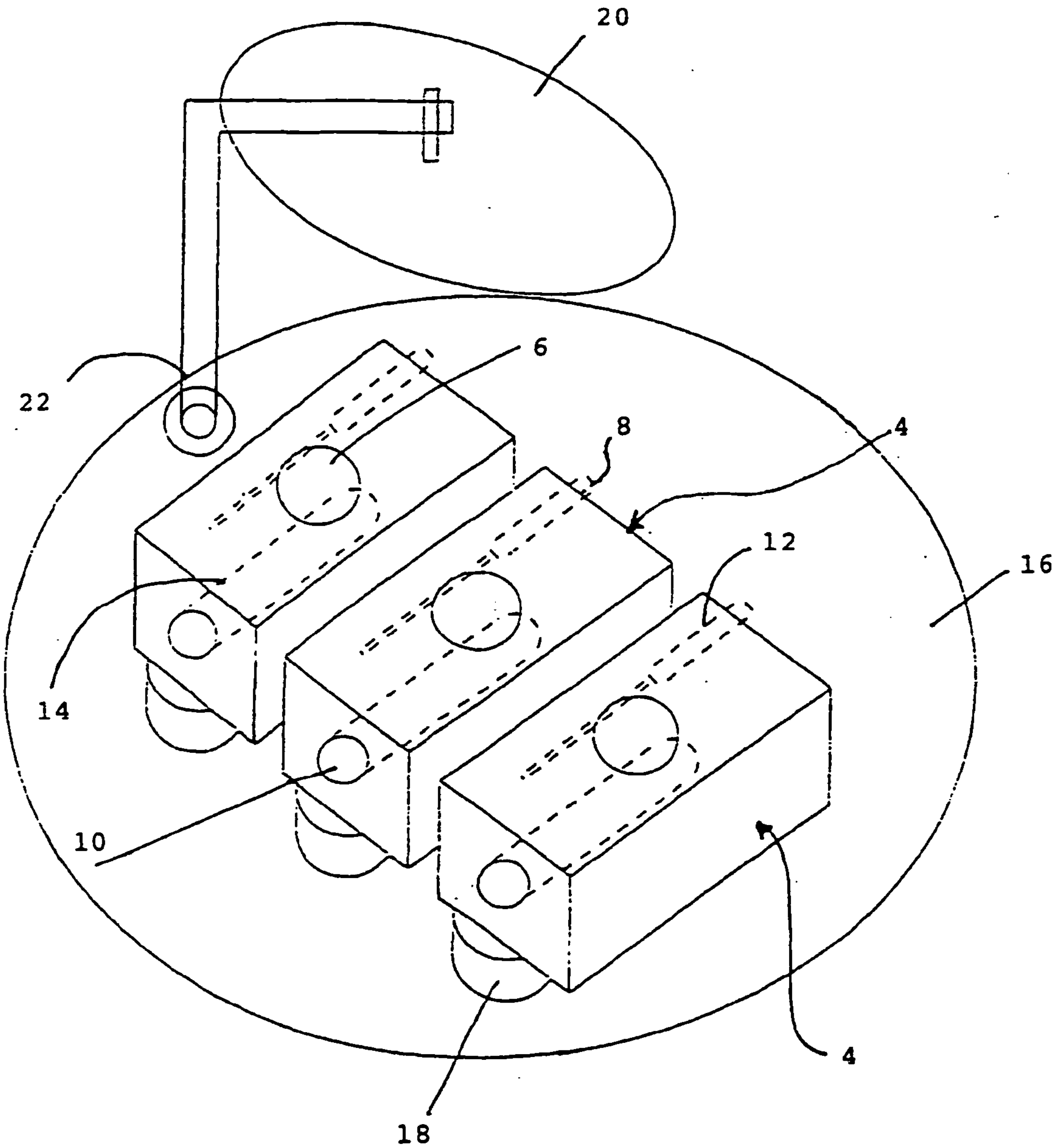
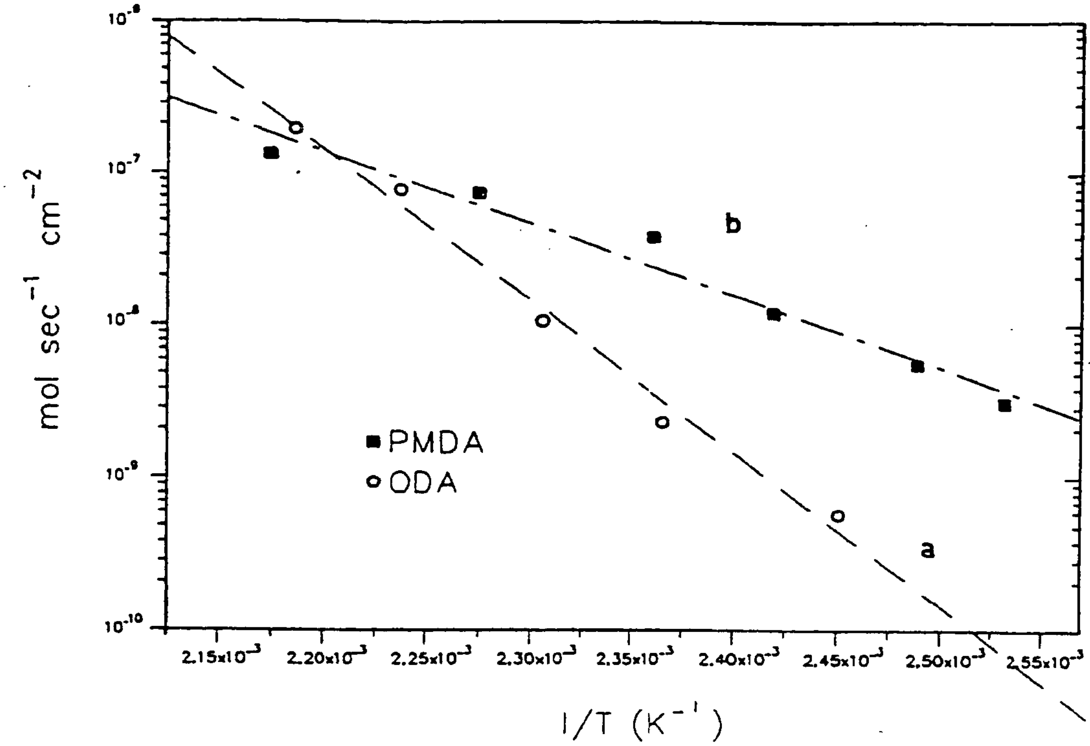


FIGURE 6



(a) 4,4' oxydianiline; (b) benzentetracarboxylic dianhydride

FIG. 7

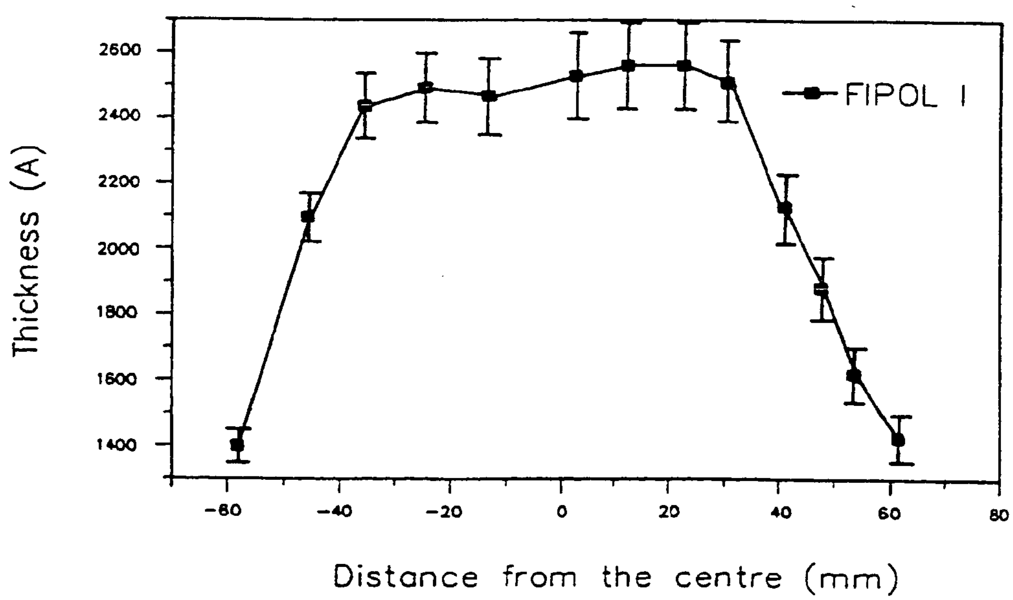


FIG. 8

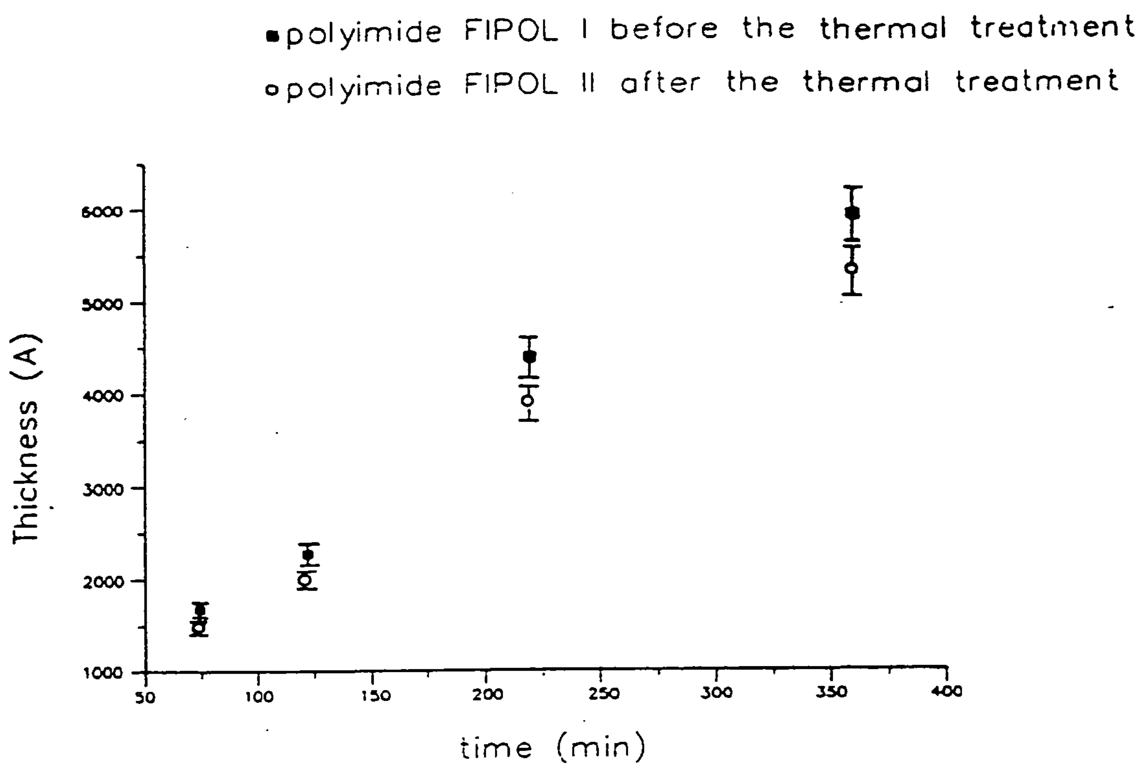


FIG. 9

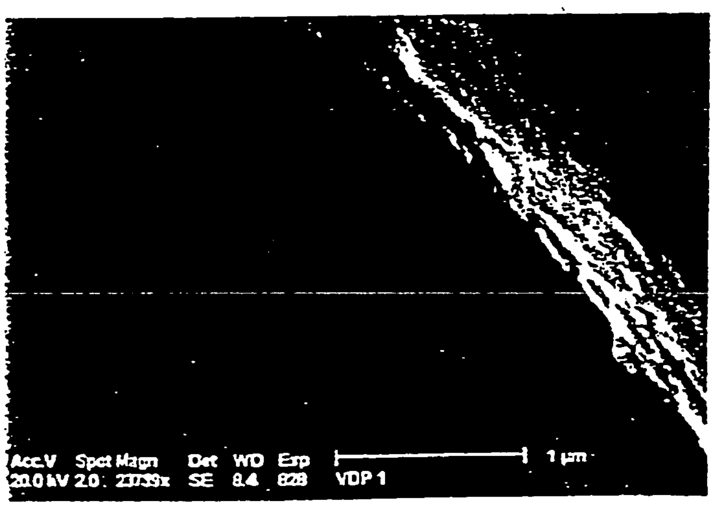


FIGURE 10

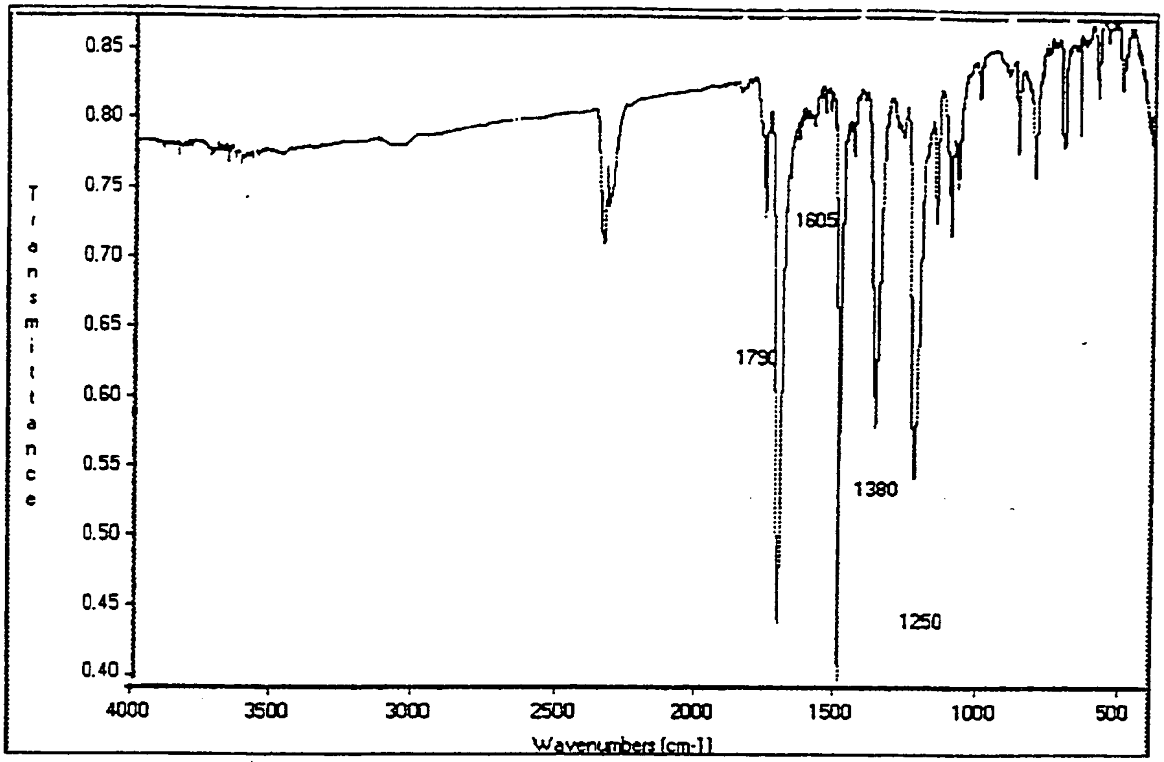


FIGURE 11

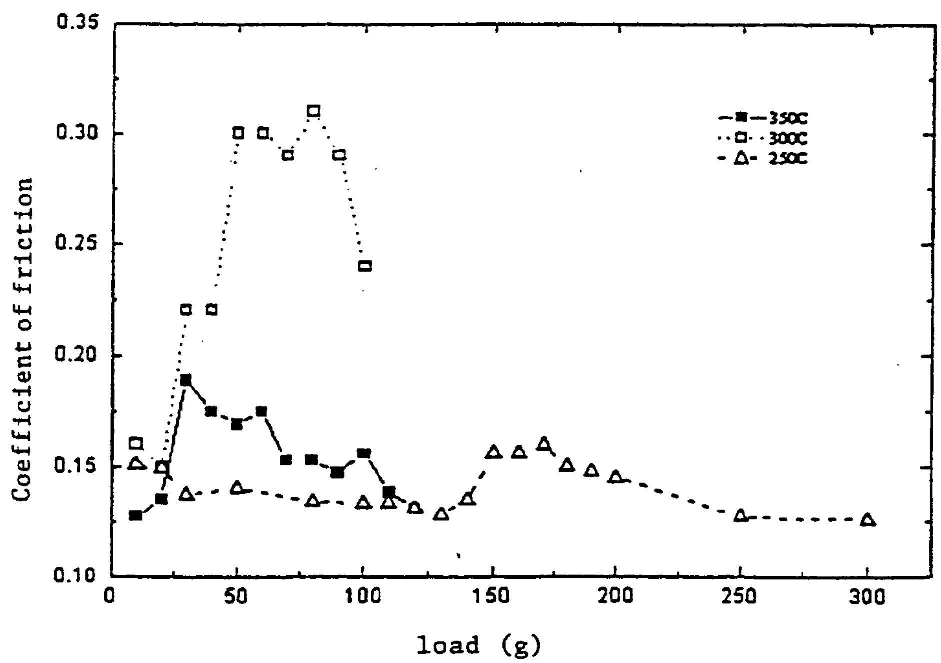


FIGURE 12

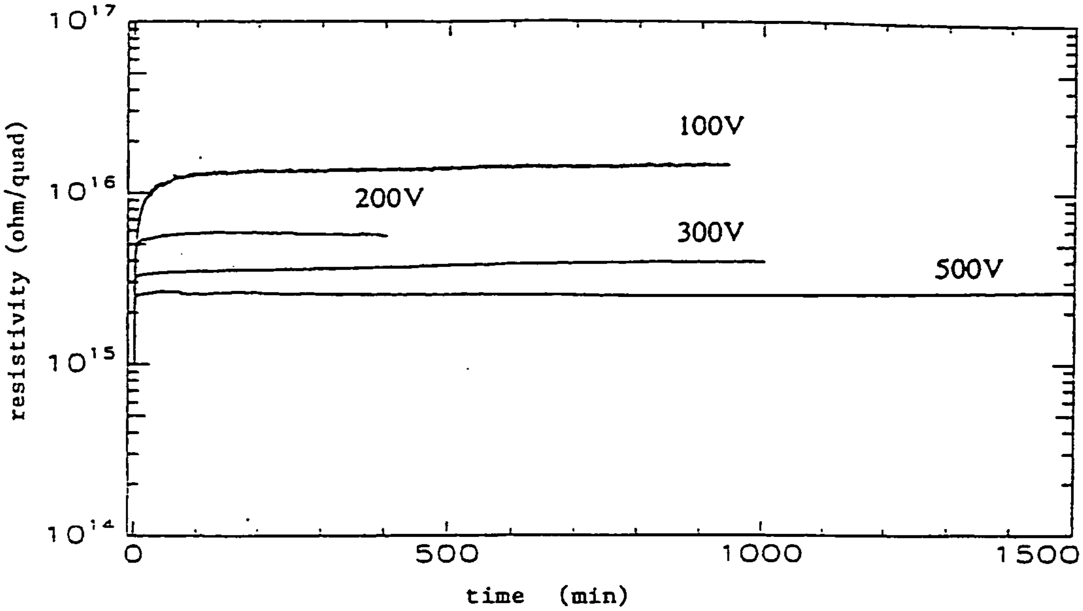


FIGURE 13

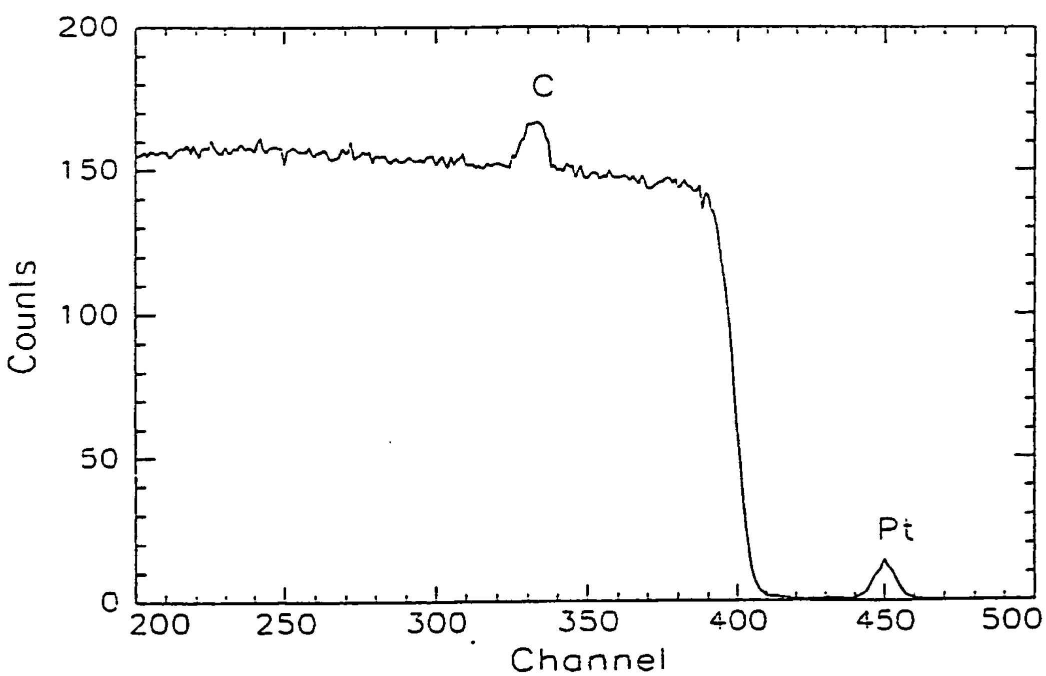


FIGURE 14

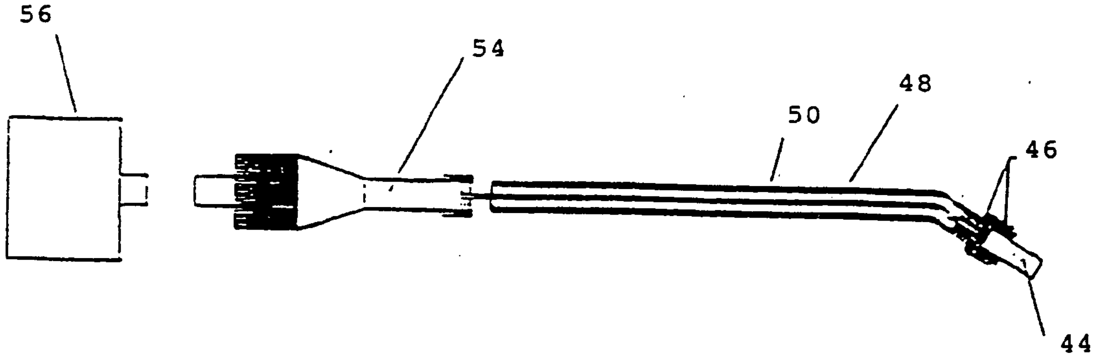


FIGURE 15

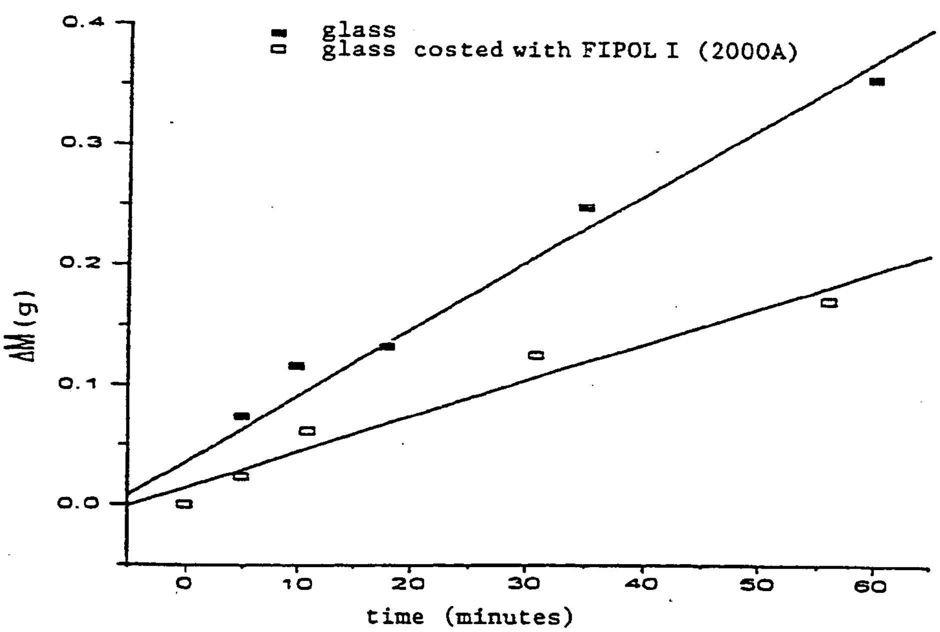


FIGURE 16

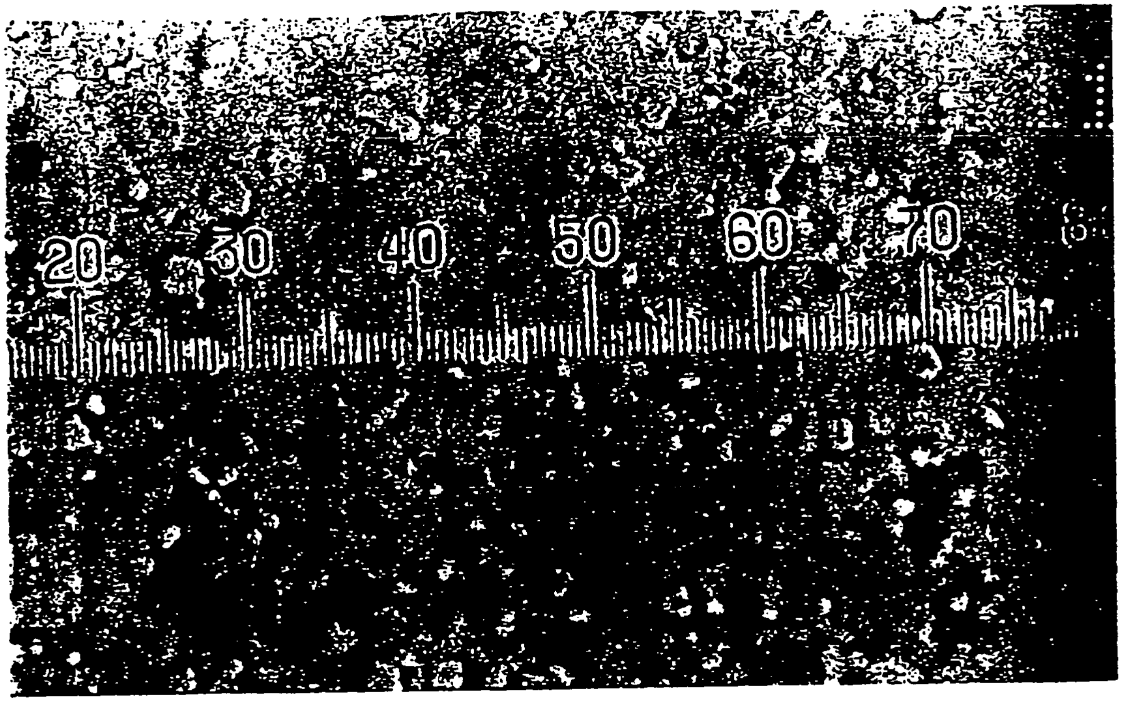


FIGURE 17A KAPTON

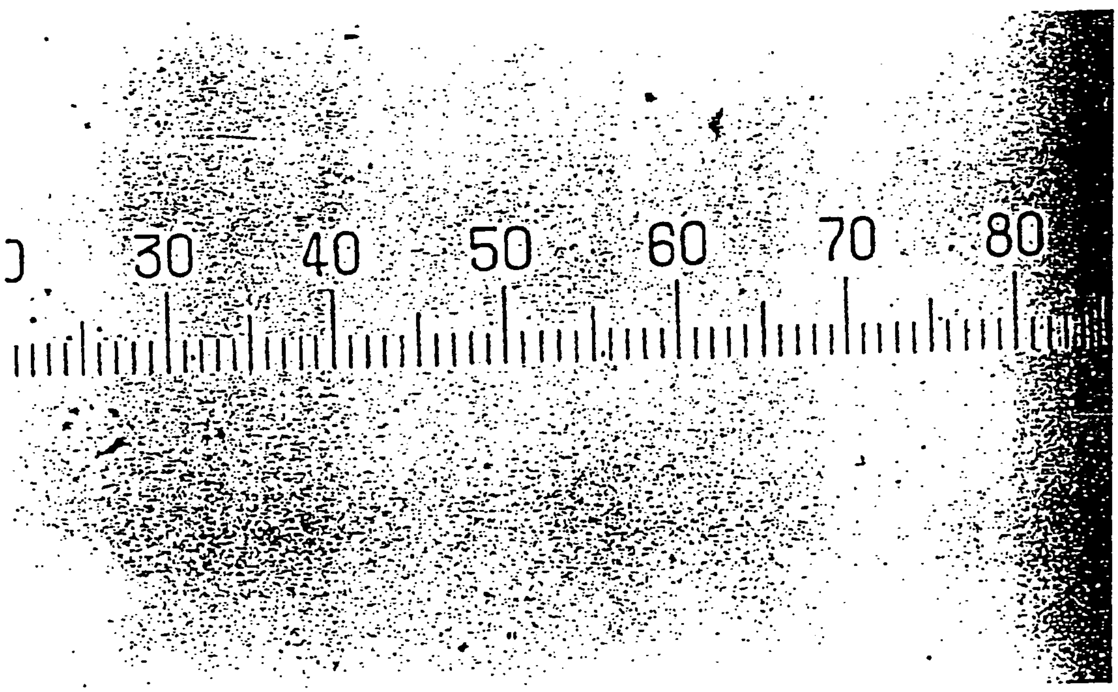


FIGURE 17B FIPOL I

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EUROPEAN SEARCH REPORT

Application Number
EP 96 83 0429

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 4, no. 3, May 1986 - June 1986, NEW YORK US, pages 369-374, XP002022479 J.R.SALEM ET AL.: "Solventless polyimide films by vapor deposition" * page 369, right-hand column * ---	1,2,5,9, 10,14,19	B05D7/24 C23C14/06 C23C14/54 C08G73/10 C09D179/08
D,X	MACROMOLECULES, vol. 22, 1989, EASTON US, pages 2944-2946, XP002022480 M. IIJIMA ET AL.: "Vapor Deposition Polymerization: A Study on Film Formation in Reaction of Pyromellitic Anhydride and Bis(4-aminophenyl) Ether" * the whole document * ---	1,2,5,9, 14	
X	EP 0 376 333 A (SHARP KK) 4 July 1990 * the whole document * ---	1-3,5,10	
X	FR 2 297 900 A (DU PONT) 13 August 1976 * the whole document * ---	14,19	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B05D C23C C08G C09D
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 060 (M-796), 10 February 1989 & JP 63 264369 A (TOSHIBA CORP), 1 November 1988, * abstract * ---	1,2,9	
X	US 5 354 636 A (ONO YOSHIYUKI ET AL) 11 October 1994 * column 34, line 40 - line 52 * --- -/--	1,2,9, 10,21	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 June 1997	Brothier, J-A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

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X	DATABASE WPI Section Ch, Week 9346 Derwent Publications Ltd., London, GB; Class A26, AN 93-362184 XP002022481 & JP 05 265 006 A (SHARP KK) , 15 October 1993 * abstract * ---	1,9	
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 132 (C-0819), 29 March 1991 & JP 03 013561 A (ULVAC CORP), 22 January 1991, * abstract * ---	1,9	
X	EP 0 278 629 A (HITACHI MAXELL) 17 August 1988 * page 4, line 7 - line 19 * ---	8,10,17, 18	
X	US 4 629 547 A (HONDA YOSHINORI ET AL) 16 December 1986 * the whole document * ---	8,21	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 051 (P-1163), 6 February 1991 & JP 02 282947 A (SEIKO EPSON CORP), 20 November 1990, * abstract * ---	8,21	
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 069 (C-569), 16 February 1989 & JP 63 259069 A (SUMITOMO ELECTRIC IND LTD), 26 October 1988, * abstract * -----	8,17,21	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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European Patent
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EP96830429

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

see sheet -B-

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☒ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respects of which search fees have been paid,

namely claims: mentioned in item 1, 5 and 7

☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.

namely claims:

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LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

Subject 1 (searched): claims 1-5, 14, and 9-11,18-19 (if dependent on the aforementioned claims).
Process for depositing thin films of polyimides through evaporation of benzentetracarboxylic dianhydride and 4-4' -oxydianiline; device for carrying out this process; polymer material prepared from the polyimide precursors such as benzentetracarboxylic dianhydride and 4-4' -oxydianiline and use as a chemically inert film against corrosion and deterioration due to environmental conditions or physical stress.

Subject 2 (not searched):: claims 1-5, 14 and 9-11,18,20 (if dependent on the aforementioned claims).
Process for depositing thin films of polyimides through evaporation of benzentetracarboxylic dianhydride and 4-4' -oxydianiline; device for carrying out this process and polymer material prepared from the polyimide precursors such as benzentetracarboxylic dianhydride and 4-4' -oxydianiline and use as detector of particles and radiations on electrical and electronic devices.

Subject 3 (not searched): claims 1-4, 6, 15 and 9-11,18-20 (if dependent on the aforementioned claims)
Process for depositing thin films of polyimides through evaporation of biphenyltetracarboxylic dianhydride and 1,4 - phenylendiamine -dianiline; device for carrying out this process; polymer material prepared from the polyimide precursors such as biphenyltetracarboxylic dianhydride and 1,4 - phenylendiamine -dianiline and use as a chemically inert film against corrosion and deterioration due to environmental conditions or physical stress or as detector of particles and radiations on electrical and electronic devices.

Subject 4 (not searched): claims 1-4, 7, 16 and 9-11,18-20 (if dependent on the aforementioned claims)
Process for depositing thin films of polyimides through evaporation of benzophenonetetracarboxylic dianhydride and tetramethyl -p- phenylendiamine;device for carrying out this process; polymer material prepared from the polyimide precursors such as benzophenonetetracarboxylic dianhydride and tetramethyl -p- phenylendiamine and use as a chemically inert film against corrosion and deterioration due to environmental conditions or physical stress or as detector of particles and radiations on electrical and electronic devices.

EPO Form Supplementary Sheet B (1996)

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LACK OF UNITY OF INVENTION

Subject 5 (searched): claims 8, 17 and 9-11, 18-20 (if dependent on the aforementioned claims)
Process for the deposition of thin film of polyimide-metal composite material and polyimide metal composite made by simultaneous evaporation of the polyimide precursors and the metal.

Subject 6 (not searched): claims 12-13
A mechanical device for continuously rotating substrate.

Subject 7 (searched): claim 21
Thin film coating caraterized by being formed of a mixture of polyimides with components not greater than 30% in weight.

The attention of the applicant is drawn on the fact that a lack of unity and/or inventive step of the process and/or polymeric material in subjects 3, 4 or 5 could lead to a non-unity a posteriori on the uses in the aforementioned subjects.

EPO Form Supplementary Sheet B (1996)